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<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C11D 1/72, 1/722, 3/22, 3/44</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/06506</b> <b>(43) International Publication Date:</b> 11 February 1999 (11.02.99)
<b>(21) International Application Number:</b> PCT/US98/14081 <b>(22) International Filing Date:</b> 7 July 1998 (07.07.98)  <b>(30) Priority Data:</b> 60/054,123 29 July 1997 (29.07.97) US 08/965,327 6 November 1997 (06.11.97) US  <b>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Applications</b> US 60/054,123 (CIP) Filed on 29 July 1997 (29.07.97) US 08/965,327 (CIP) Filed on 6 November 1997 (06.11.97)  <b>(71) Applicant (for all designated States except US):</b> PAINTEX INTERNATIONAL CORPORATION [US/US]; 664 Topeka Avenue, Ventura, CA 93004 (US).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> HOPFSTOCK, Herbert [DE/DE]; Konigskrug 1, D-29614 Soltau (DE).  <b>(74) Agent:</b> JACOBS, Marvin, E.; Koppel & Jacobs, Suite 215, 2151 Alessandro Drive, Ventura, CA 93001 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PAINT REMOVAL COMPOSITION AND SYSTEM  <b>(57) Abstract</b>  An environmentally safe composition for removing paint and other materials deposited on a substrate, such as graffiti sprayed, on a prepainted surface including a synergistic combination of 2 to 20 parts by weight of an anionic and/or nonionic poly alkoxylated surfactant such as a poly alkoxylated alkyl ethercarboxylic acid, poly alkoxylated alkyl ethercarboxylic ester, poly alkoxylated alkyl ethercarboxylate, poly alkoxylated fatty acid, poly alkylene glycol ester, poly alkoxylated alcohol and 10 to 90 parts by weight of a poly alkylene glycol alkyl ether solvent. Preferably, the carbon content of the repeating unit of the alkoxylated group in both the surfactants and solvents is the same or differ by no more than 3 carbon atoms. 5 to 70 parts by weight of an organic solvent selected from a polar aprotic solvent and/or a hydrocarbon solvent, 3 to 25 parts by weight of a poly alkylene glycol alkyl acetate, 0.1 to 5.0 parts by weight of a hydroxyalkylated cellulose thickener and 0.1 to 2.0 parts by weight of a substance to adjust pH to between 5.0 and 7.5 may optionally be present.		

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## ***DESCRIPTION***

### **PAINT REMOVAL COMPOSITION AND SYSTEM**

#### Cross-Reference to Related Application

This application is a complete application of U.S. Provisional Application Serial No. 60/054,123 filed July 29, 1997 and is disclosed in Disclosure Document No. 413,959 filed July 17, 1997 retention of Disclosure Document No. 413,959 is requested.

#### Technical Field

This invention relates to compositions for removing paint and, more particularly this invention relates to an environmentally safe paint removal composition based on organic surfactants and polymeric organic solvents.

#### Background of the Invention

Traditionally, paint removers have been based on organic solvents. However as the toxic and environmental effects of volatile organic compounds ( VOC ) and halogenated solvents have been recognized, regulations have been promulgated to remove these ingredients from solvents. The reformulated paint remover products on the market are difficult to use and are not very effective in removing paint from a surface. This is especially true for granular, rough surfaces. Some of the products also contain metal salts impurities such as nitrates, sulfates or phosphates which can irritate skin and are not suitable for normal disposal. The products must be disposed of as hazardous waste. Also, prior paint remover products have high or low pH again causing irritation to skin and waste disposal concerns. Some products contain organic solvents having low flash points, high contents of VOC and are flammable. Data on some organic solvents used in paint removers follows :

Compound	Kp [ °C ]	Fla.p. [ °C ]	d(20°C) [ g/ml ]	Vap.p. [ mmHg ]	Solubility in H <sub>2</sub> O	Toxicity
acetone	56	-20	0,79	180	complete	F
1,4-dioxane	101	12	1,03	29	complete	F
isophorone	215	86	0,92	0.7	1.2 %	X <sub>i</sub>
methylene chloride	40	none	1,32	350	2.0 %	X <sub>n</sub>
benzene	80	-11	0,88	75	none	F, T
toluene	111	6	0,87	22	none	F, X <sub>n</sub>

F = flammable    T = toxic    X<sub>i</sub> = irritant    X<sub>n</sub> = low irritant

There is an epidemic of spray painting graffiti onto the walls of buildings, fences, traffic signs, sidewalks, etc. in the United States. Many of the walls are finished with a rough, relieved finish. The spray paint is propelled into the relief of the wall and is very difficult to remove except by sand blasting. Most of the time, the graffiti is not removed. It is covered with a patch of paint. Usually, the patches of paint do not match the paint surrounding and adjacent the patch creating an unattractive pattern of different colored areas on the wall.

Another environmental problem has created demand for paint removal. Many old buildings contain surface painted with paints that contain lead. Studies have demonstrated that children who live in housing containing lead paint have high levels of lead in their blood which can interfere with brain development.

### ***STATEMENT OF THE INVENTION***

The invention comprises a composition for removing paint, particularly graffiti, from surfaces wherein the composition contains non-toxic and non-irritant ingredients including a synergistic combination of anionic and / or nonionic poly alkoxyated surfactants such as a poly alkoxyated alkyl ethercarboxylic acid, poly alkoxyated alkyl ethercarboxylic ester, poly alkoxyated alkyl ethercarboxylate, poly alkoxyated fatty acid, poly alkylene glycol ester, poly alkoxyated alcohol and a lower poly alkylene glycol alkyl ether having a repeating unit containing 2-9 carbon atoms wherein 5 to 70 % by weight of a polar aprotic solvent and / or a hydrocarbon solvent is present.

The paint removing compositions of the invention do not contain nitrate, sulfate, phoshate impurities or halogenated solvents. It is further noted that the compositions have a neutral pH, are completely soluble in water or completely emulsifiable, although water neutralizes the synergistic effect. The synergism is also diminished as the alkoxy unit of the surfactants and / or the solvents of poly alkylene glycol alkyl ether increases.

#### List of References

<u>PATENT NO.</u>	<u>PATENTEE</u>
4,780,235	Jackson
4,863,525	Goel et al.
5,308,527	Lallier et al.
5,332,526	Stanley
5,346,640	Leys
5,415,800	Motsenbocker
5,604,196	Weltman et al.
5,629,277	Plishka

#### Statement of the Prior Art

Leys' discloses a composition for removing graffiti, which is formulated using propylene carbonate, isocetyl alcohol, N-methylpyrrolidone and a dipropylene glycol monomethyl ether acetate. A cellulose thickener may be present. Column 7, line 3, et seq., contains a brief statement regarding synergism.

The patent to Lallier et al. discloses a paint removing composition particularly utilizing an aprotic polar solvent.

The remaining patents are of varying degrees of general interest.

### Detailed Description of the Invention

The paint remover composition of the invention has a high flash point  $\geq 90$  °C, a high boiling point  $\geq 150$  °C, a very low content of volatile organic compounds (  $\text{VOC} \leq 0.5$  g/l ) and a very low vapor pressure (  $\text{Vap.p.}^{20^\circ\text{C}} \leq 0.5$  mm Hg ). The pH is preferably neutral but can be slightly acid ( pH 5.0 - 7.5 ). The composition is non-toxic, non-irritating, non-flammable and is biodegradable. The solvation activity is believed to proceed as a result of a synergistic combination between poly alkoxylated anionic and / or nonionic surfactants portions and solvents of poly alkylene glycol alkyl ether in which both the surfactant and solvent have similar poly alkoxylated chains.

The solvation activity appears to proceed due to the matched polymeric surfactants initializing an intermolecular reaction with the polymers in the paint. The overlapping electrostatic fields contribute to separation of polymeric chains in the polymeric film former of the paint and possibly to some depolymerization to break cross-links and reduce chain length of the polymer chains as the paint dissolves.

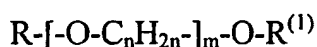
The synergistic effect and solvation activity are not present when water is added to the composition. Water hydrates the surfactants forming sheaths which isolate the surfactants from each other and form the polymer molecules in the film former of the paint. However, water can be used to deactivate the paint remover composition such as after removal of paint or to control an accidental spill.

The overlapping electrostatic fields are enhanced by the addition of nucleophilic-aprotic substances. The viscosity of the composition can be increased by adding a compatible thickener, preferably a hydroxyalkylated cellulose in the range of 0.1 to 5.0 % by weight. These thickeners have been found to not affect the synergistic solvation effect. When the pH is too low, a base such as an amine, suitably a di- or triethanolamine in the amount of 0.1 to 2.0 % by weight can be added to the composition.

The paint remover composition of the invention can be used to remove other materials from substrates such as ink, brushed or sprayed paints, varnishes, resins, enamels, wax, glue etc.

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The synergism is demonstrated by a combination of 2 to 20 parts by weight of a poly alkoxyated surfactant ( poly alkoxyated alkyl ethercarboxylic acid, poly alkoxyated alkyl ethercarboxylic ester, poly alkoxyated alkyl ethercarboxylate, poly alkoxyated fatty acid, poly alkylene glycol ester, poly alkoxyated alcohol etc. ) thereof such as those of the formula :

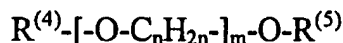


where R is a hydrocarbon group containing 1-30 carbon atoms such as alkyl, alkylaryl and fatty alkyl, preferably fatty alkyl containing 8-24 carbon atoms, where  $R^{(1)}$  is a special group ( see below ), n is 2,3 or 4, m is at least 4 such that the anionic and / or nonionic surfactant is liquid, usually from 2 to 20, preferably from 2 to 10;

<b>poly alkoxyated surfactants</b> $R-[-O-C_nH_{2n}-]_m-O-R^{(1)}$ R = alkyl, alkylaryl, fatty alkyl $R^{(1)}$ = special group    n = 2 ... 4    m = 4 ... ∞	
Chemical name	Special formula
poly alkoxyated alkyl ethercarboxylic acid	$R-[-O-C_nH_{2n}-]_m-O-CH_2COOH$ $R^{(1)} = -CH_2COOH$
poly alkoxyated alkyl ethercarboxylic ester	$R-[-O-C_nH_{2n}-]_m-O-CH_2COOR^{(2)}$ $R^{(1)} = -CH_2COOR^{(2)}$ $R^{(2)} = \text{alkyl, alkylaryl, fatty alkyl}$
poly alkoxyated alkyl ethercarboxylate	$R-[-O-C_nH_{2n}-]_m-O-CH_2COO^-M^+$ $R^{(1)} = -CH_2COO^-M^+$ , $M^+$ = counterion ( $Na^+$ , $K^+$ , $NH_4^+$ , $Mg^{2+}$ , $TEA^+$ , etc. )
poly alkoxyated fatty acid, poly alkylene glycol ester	$R-[-O-C_nH_{2n}-]_m-O-COR^{(3)}$ $R^{(1)} = -COR^{(3)}$ $R^{(3)} = \text{alkyl, alkylaryl, fatty alkyl or -H}$
poly alkoxyated alcohol	$R-[-O-C_nH_{2n}-]_m-OH$ $R^{(1)} = -H$
It is also possible, that the alkoxyated groups are mixed EO/PO block copolymers $[-O-C_nH_{2n}-]_m \Rightarrow [-O-CH_2CH_2-]_x[-O-CH(CH_3)CH_2-]_y$ $x + y = m$	

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and 10-90 parts by weight of a poly alkylene glycol alkyl ether of the formula :



where  $R^{(4)}$  and  $R^{(5)}$  are individually selected from the group consisting of H and alkyl of 1-10 carbon atoms, n is from 2 to 6, preferably from 2 to 4 and m is 2 to 10, preferably from 2 to 4.

**poly alkylene glycol alkyl ether**  $R^{(4)}-[-O-C_nH_{2n}]_m-O-R^{(5)}$

$R^{(4)}, R^{(5)} = -H, \text{ alkyl} \quad n = 2 \dots 6 \quad m = 2 \dots 10$

The synergistic solvent activity decreases as the chain length of alkylene ether group increases and is absent in ethers having a carbon length of 5 or more.

Other optional ingredients are poly alkoxyated alkyl acetates in an amount from 0-30 % by weight, preferably 5-25 % by weight, nucleophilic-aprotic solvents in an amount from 0-70 % by weight, preferably 10-60 % by weight, 0-2 % by weight of a base such as a Group I or Group II metal hydroxide or a polyamine such as di- or triethanolamine and 0-5 % by weight, preferably 1-3 % by weight, of a thickening agent such as hydroxyalkyl cellulose in which the alkyl contains from 1-6 carbon atoms.



The following formulations provide safe and effective paint removing compositions :

Compound	Formula and chemical range	Range in % by weight
<b>MAJOR INGREDIENTS</b>		
poly alkoxyated surfactants ( see page 5 )	$R-[-O-C_nH_{2n}-]_m-O-R^{(1)}$ R = alkyl, alkylaryl, fatty alkyl R <sup>(1)</sup> = special group n = 2 ... 4 m = 4 ... ∞	2 - 20
poly alkylene glycol alkyl ether ( see page 6 )	$R^{(4)}-[-O-C_nH_{2n}-]_m-O-R^{(5)}$ R <sup>(4)</sup> , R <sup>(5)</sup> = -H, alkyl n = 2 ... 6 m = 2 ... 10	10 - 90
<b>OPTIONAL INGREDIENTS</b>		
poly alkylene glycol alkyl acetate	$R^{(6)}-[-O-C_nH_{2n}-]_m-O-CH_2COOR^{(7)}$ R <sup>(6)</sup> , R <sup>(7)</sup> = -H, alkyl n = 2 ... 6 m = 2 ... 10	3 - 25
nucleophilic-aprotic substances	ethylene or propylene carbonate, dimethylsulfoxide DMSO, N-methyl-2-pyrrolidinone, γ-butyrolactone etc.	5 - 70
hydrocarbon solvent	all isomers of mono-, di-, tri- or tetraalkylbiphenyl ( alkyl = -C <sub>n</sub> H <sub>2n+1</sub> ; n = 1 ... 5 )	5 - 70
pH-buffer substances	KOH, di- or triethanolamine	0.1 - 2
thickening agent	hydroxyalkyl cellulose	0.1 - 5

The first optional ingredients are organic solvents selected from nucleophilic-aprotic material and / or a hydrocarbon solvent.

Ingredients for use in the composition of the invention were tested for boiling point [ Kp in °C ], flash point [ Fla.p. in °C ], density [ d<sub>20°C</sub> in g/ml ], vapor pressure [ Vap.p in mmHg ], solubility in water and toxicity, results follow :

Tested Compound	Kp [ °C ]	Fla.p. [ °C ]	d(20°C) [ g/ml ]	Vap.p. [ mmHg ]	Solubility in H <sub>2</sub> O	Toxicity
<b>R-[O-CH<sub>2</sub>CH<sub>2</sub>]<sub>n</sub>OCH<sub>2</sub>COOH ethoxylated alkyl ethercarboxylic acids</b>						
R = -CH <sub>2</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> ; n = 9 Oleylethercarboxylic acid ( 9 EO )	> 200	> 100	-	< 0.01	complete	none
R = -CH <sub>2</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub> ; n = 10 lauryl ethercarboxylic acid ( 10 EO )	> 200	> 100	-	< 0.01	complete	none
R = -CH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> ; n = 8 octyl ethercarboxylic acid ( 8 EO )	> 200	> 100	-	< 0.01	complete	none
R = -CH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> ; n = 7 hexyl/octyl ethercarboxylic acid ( 7 EO )	> 200	> 100	-	< 0.01	complete	none
R = -CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2/6</sub> CH <sub>3</sub> ; n = 5 butyl/octyl ethercarboxylic acid ( 5 EO )	> 200	> 100	-	< 0.01	complete	none
<b>R-[O-CH<sub>2</sub>CH<sub>2</sub>]<sub>n</sub>OCOR' ethoxylated fatty acids, glycols and PEG esters</b>						
PEG - 8 Oleate	> 200	> 100	-	< 0.01	complete	none
Castor Oil + 15 EO	> 200	> 100	-	< 0.01	complete	none
<b>R-[O-(-CH<sub>2</sub>)<sub>n</sub>]<sub>m</sub>-O-R' poly alkylene glycol alkyl ethers</b>						
R = -H; R' = -CH <sub>3</sub> ; n = 2; m = 2 diethylene glycol monomethyl ether	194	91	1.03	0.2	complete	T
R = R' = -CH <sub>3</sub> ; n = 2; m = 2 diethylene glycol dimethyl ether	162	53	0.95	5.3	complete	T
R = -H; R' = -C <sub>2</sub> H <sub>5</sub> ; n = 2; m = 2 diethylene glycol monoethyl ether	202	94	0.99	0.1	complete	none
R = R' = -C <sub>2</sub> H <sub>5</sub> ; n = 2; m = 2 diethylene glycol diethyl ether	189	90	0.91	0.5	complete	none
R = -H; R' = -C <sub>3</sub> H <sub>7</sub> ; n = 2; m = 2 diethylene glycol monopropyl ether	-	-	-	-	complete	none
R = R' = -C <sub>3</sub> H <sub>7</sub> ; n = 2; m = 2 diethylene glycol dipropyl ether	-	-	-	-	complete	none
R = R' = -C <sub>4</sub> H <sub>9</sub> ; n = 2; m = 2 diethylene glycol monobutyl ether	228	105	0.95	0.2	10 %	X <sub>i</sub>
R = -H; R' = -C <sub>4</sub> H <sub>9</sub> ; n = 2; m = 2 diethylene glycol dibutyl ether	256	118	0.88	< 0.01	0.3 %	X <sub>i</sub>
R = -H; R' = -CH <sub>3</sub> ; n = 2; m = 3 triethylene glycol monomethyl ether	250	133	1.04	0.1	complete	none
R = R' = -CH <sub>3</sub> ; n = 2; m = 3 triethylene glycol dimethyl ether	216	113	0.99	0.02	complete	none
R = -H; R' = -CH <sub>3</sub> ; n = 2; m = 4 tetraethylene glycol monomethyl ether	-	-	-	-	complete	none
R = R' = -CH <sub>3</sub> ; n = 2; m = 4 tetraethylene glycol dimethyl ether	275	> 130	1.01	< 0.01	complete	none
R = R' = -CH <sub>3</sub> ; n = 2; m = 4 ... 10 polyethylene glycol dimethyl ether	> 300	> 130	1.04	< 0.01	complete	none
R = -H; R' = -CH <sub>3</sub> ; n = 3; m = 2 dipropylene glycol monomethyl ether	189	80	0.95	0.5	complete	none
R = R' = -CH <sub>3</sub> ; n = 3; m = 2 dipropylene glycol dimethyl ether	-	-	-	-	complete	none

F = flammable T = toxic X<sub>i</sub> = irritant X<sub>n</sub> = low irritant

Tested Compound	Kp [ °C ]	Fla.p. [ °C ]	d(20°C) [ g/ml ]	Vap.p. [ mmHg ]	Solubility in H <sub>2</sub> O	Toxicity
R = -H; R' = -C <sub>2</sub> H <sub>5</sub> ; n = 3; m = 2 dipropylene glycol monoethyl ether	-	-	-	-	complete	none
R = -H; R' = -C <sub>2</sub> H <sub>5</sub> ; n = 3; m = 2 dipropylene glycol monopropyl ether	-	-	-	-	complete	none
R = -H; R' = -C <sub>4</sub> H <sub>9</sub> ; n = 3; m = 2 dipropylene glycol monobutyl ether	-	-	-	-	-	none
R = -H; R' = -CH <sub>3</sub> ; n = 3; m = 3 tripropylene glycol monomethyl ether	242	110	0,96	0,02	complete	none
R = -H; R' = -C <sub>4</sub> H <sub>9</sub> ; n = 3; m = 3 tripropylene glycol monobutyl ether	-	-	-	-	-	none
nucleophilic-aprotic substances						
ethylene carbonate	248	-	-	-	21 %	none
propylene carbonate	241	135	1,21	0.03	24 %	X <sub>i</sub>
γ-butyrolactone	205	104	1,13	1,1	complete	X <sub>n</sub>
N-methyl-2-pyrrolidinone; NMP	202	91	1,03	0.2	complete	X <sub>i</sub>
dimethyl sulfoxide; DMSO	189	95	1,10	0,5	complete	none
1,3-dimethyltetrahydro-2(1H)-pyrimidinone	247	120	1,06	-	-	X <sub>n</sub>
1,3-dimethyl-2-imidazolidinone	225	93	1,06	-	-	none
other compounds who are possible to add						
[2-(2-butoxyethoxy)-ethyl]-acetate	246	102	0,98	< 0,01	6.5 %	none
diethyl acetonyl succinate	-	> 110	1,07	-	-	none
$R_1OOC-[CH_2]_n-COOR_1$ $R_1 = \text{alkyl}$ n = 2    Dialkylsuccinate,    n = 3    Dialkylglutarate,    n = 4    Dialkyladipate						
dimethyl succinate; $R_1 = -CH_3$ ; n = 2	196	90	1.12	0.2	7.5 %	X <sub>i</sub>
dimethyl glutarate; $R_1 = -CH_3$ ; n = 3	212	107	1.09	0.07	4.3 %	-
dimethyl adipate; $R_1 = -CH_3$ ; n = 4	-	102	1.06	-	-	-
diethyl succinate; $R_1 = -C_2H_5$ ; n = 2	216	80	1.04	-	-	-
diethyl glutarate; $R_1 = -C_2H_5$ ; n = 3	237	-	1.02	-	-	-
diethyl adipate; $R_1 = -C_2H_5$ ; n = 4	242	> 100	1.01	-	-	-
diisobutyl succinate; $R_1 = -C_4H_7$ ; n = 2	-	-	-	-	-	-
diisobutyl glutarate; $R_1 = -C_4H_7$ ; n = 3	-	-	-	-	-	-
diisobutyl adipate; $R_1 = -C_4H_7$ ; n = 4	-	-	-	-	-	-

F = flammable    T = toxic    X<sub>i</sub> = irritant    X<sub>n</sub> = low irritant

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The following compositions were prepared :

Example No. 1

<i>No. 1 ( Classic )</i>	
5,0 %	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2-[\text{-O-CH}_2\text{CH}_2\text{-}]_9\text{-OCH}_2\text{COOH}$ oleyl ethercarboxylic acid ( 9 EO )
19,2 %	$\text{CH}_3-[\text{-O-CH}_2\text{CH}_2\text{-}]_3\text{-O-CH}_3$ triethylene glycol dimethyl ether ( triglyme )
25,0 %	$\text{CH}_3-[\text{-O-CH}_2\text{CH}_2\text{-}]_4\text{-O-CH}_3$ tetraethylene glycol dimethyl ether ( tetraglyme )
25,0 %	$\text{CH}_3-[\text{-O-CH}_2\text{CH}_2\text{-}]_n\text{-O-CH}_3$ polyethylene glycol dimethyl ether ( polyglyme )
10,0 %	$\text{H}-[\text{-O-CH}_2\text{CH}_2\text{CH}_2\text{-}]_2\text{-O-CH}_3$ dipropylene glycol monomethyl ether
5,0 %	4-methyl-1,3-dioxolan-2-on ( propylene carbonate )
0,3 %	triethanolamine ( TEA )
0,5 %	hydroxypropyl cellulose

The composition exhibited very strong performance and was found to remove spray paints including those based on polyurethane from surfaces. The composition can be used on stone, concrete, glass and metal surfaces. This composition will also remove paint from other surfaces and can dissolve plastic. Care should be taken to avoid applying this composition to surrounding paint and plastic parts.

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Example No. 2

<i>No. 2 ( Special )</i>	
5.0 %	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2-[-\text{O}-\text{CH}_2\text{CH}_2-]_9-\text{OCH}_2\text{COOH}$ oleyl ethercarboxylic acid ( 9 EO )
81.7 %	$\text{H}-[-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-]_2-\text{O}-\text{CH}_3$ dipropylene glycol monomethyl ether
12.5 %	4-methyl-1,3-dioxolan-2-on ( propylene carbonate )
0.3 %	triethanolamine ( TEA )
0.5 %	hydroxypropyl cellulose





















This composition, though high performance, is not as strong as the composition of Example No. 1. It will remove spray paints from most surfaces and will not affect an underlying film of paint. For example, graffiti can be removed from printed utility boxes, carpets, upholstery etc..

This product must remain on the graffiti or other stain less than 5 minutes, because plastics, the underlying paints and man-made fibres can be attacked if in contact with the composition for a longer period of time.

## 12








The compositions of Example No. 1 and No. 2 were varied by substituting poly alkylene glycol alkyl ether of increasing carbon content.

The solvation power of the paint remover composition is presented in the following table :

Name of the alkylene glycol alkyl ether	Level of power Minimum Maximum
diethylene glycol monomethyl ether	
diethylene glycol dimethyl ether	
diethylene glycol monoethyl ether	
diethylene glycol diethyl ether	
diethylene glycol monopropyl ether	
diethylene glycol dipropyl ether	
diethylene glycol monobutyl ether	
diethylene glycol dibutyl ether	
triethylene glycol monomethyl ether	
triethylene glycol dimethyl ether	
tetraethylene glycol monomethyl ether	
tetraethylene glycol dimethyl ether	
polyethylene glycol dimethyl ether	
dipropylene glycol monomethyl ether	
dipropylene glycol dimethyl ether	
dipropylene glycol monoethyl ether	
dipropylene glycol monopropyl ether	
dipropylene glycol monobutyl ether	
tripropylene glycol monomethyl ether	
tripropylene glycol monobutyl ether	

## 13

The compositions of Example No. 1 and No. 2 were varied by substituting various nucleophilic-aprotic solvents. Results follow :

Name of the nucleophilic-aprotic solvent	Level of power	
	Minimum	Maximum
ethylene carbonate		
propylene carbonate		
$\gamma$ -butyrolactone		
N-methyl-2-pyrrolidinone; NMP		
dimethyl sulfoxide; DMSO		
1,3-dimethyltetrahydro-2(1H)-pyrimidinone		
1,3-dimethyl-2-imidazolidinone		

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Paint removal with the composition of the invention is very simple. It will remove most spray paints ( graffiti ) but also ink, brushed or sprayed paints, varnishes, resins, enamels, wax, glue, etc.. The paint remover product of the invention is environmentally sensitive and accomplishes the removal of paint or other substances in a simple, safe procedure.

The paint remover compositions consist of a finely balanced blend of anionic and / or nonionic surfactants with synergistic effects that operates with polymeric organic ether, ester and ketonic compounds. The products do not contain nitrate, sulphate, phosphate salts or other impurities such as halogenated solvents. They have neutral pH, are completely soluble in water or completely emulsifiable, having a high flash point ( Fla.p.  $\geq 90$  °C ), a high boiling point ( Kp  $\geq 150$  °C ), a very low content of volatile organic compounds ( VOC  $\leq 0.5$  g/l ) and a very low vapor pressure ( Vap.p.<sup>20°C</sup>  $\leq 0.5$  mm Hg ), they are non-toxic, non-irritating, non-flammable and are biodegradable.

The paint remover of the invention can be used on nearly all surfaces safely. The composition has a high efficiency for each gallon it is possible to remove paint on approximately 40 yd<sup>2</sup>, depending on the kind of surfaces ( textures from smooth to porous ) and the constitution of the paint ( age, thickness, quality ). The products of the invention are far superior to all previous paint removal products.

The composition can simply be sprayed or brushed on surfaces that need paint removing. Leave it in place for 2 to 10 minutes, depending on the surfaces and constitutions of the paint ( see above ). After processing, it can be cleaned by rubbing off with a towel, sponge, brush, or preferably by means of a high pressure water sprayer ( 1,000 to 2,000 psi ). It is important to wash the residue of the paint remover off with water to deactivate the solvent activity. Old or thick paint may require the process to be repeated two or three times. For thick paints it is helpful to use a wire brush before processing, to rough up the surface so that the paint removal products can penetrate faster. The composition should not be used at temperatures below 35 °F and outside in the rain. It is prudent to pre-test the surfaces for possible reactions with the products.



*15*

The composition of the invention can also contain minor amounts of optional ingredients suitably as dyes or pigments enhancing substances and preservatives each in an amount effective to provide the desired effect, along with a fragrance. The composition of the invention can also be used to remove fingernail polish. Cosmetic compositions can contain a skin protectant such as glycerine or diglycerol.

It is to be realized that only preferred embodiments of the invention have been described and that numerous substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

## CLAIMS

1. A non-toxic, non-irritating, non-flammable composition for cleaning surfaces, absent chlorinated solvents and having a low VOC comprising in combination :

A synergistic combination of an anionic and / or nonionic poly alkoxylated surfactant and a lower poly alkylene glycol alkyl ether having a repeating unit containing 2-9 carbon atoms.

2. A composition according to claim 1 further comprising an organic solvent selected from at least one of the group consisting of a polar aprotic solvent and a hydrocarbon solvent each present in an amount from 5 to 70 % by weight of the composition.

3. A composition according to claim 1 in which the poly alkoxylated surfactant is selected from the group consisting of a poly alkoxylated alkyl ether compound selected from the group consisting of carboxylic acid, carboxylic ester and carboxylate salt; a poly alkoxylated fatty acid, poly alkylene glycol ester and poly alkoxylated alcohol.

4. A composition according to claim 3 in which the surfactant contains a repeating alkoxy unit containing 2-9 carbon atoms.

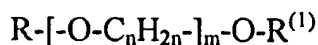
5. A composition according to claim 1 further including a thickener in an amount effective to form a gel-like composition.

6. A composition according to claim 4 in which the thickener is a hydroxy lower alkyl cellulose present in an amount 0.1 to 5.0 % by weight.

7. A composition according to claim 1 in which the composition further contains an additive effective to adjust the pH of the composition to between 5.0 and 7.5.

8. A composition according to claim 6 in which the pH adjusting additive is a Group I or Group II metal hydroxide or an amine selected from the group consisting of diethanolamine and triethanolamine present in an amount of 0.1 to 2.0 % by weight.

9. A composition according to claim 1 in which the composition has a flash point  $\geq 90$  °C, a boiling point  $\geq 150$  °C, a VOC  $\leq 0.5$  g/l and a vapor pressure at 20 °C of  $\leq 0.5$  mm Hg.
10. A composition according to claim 9 in which the composition contains 2 to 20 parts by weight of a poly alkoxyated surfactant and 10 to 90 parts by weight of a poly alkylene glycol alkyl ether.
11. A composition according to claim 10 in which the poly alkoxyated surfactant is selected from compounds of the formula :



where R is alkyl, alkylaryl and fatty alkyl containing 1-30 carbon atoms, n is 2,3 or 4, m is at least 4 and  $R^{(1)}$  is selected from the group consisting of :

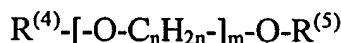
$-\text{CH}_2\text{COOH}$	( a poly alkoxyated alkyl ethercarboxylic acid )
$-\text{CH}_2\text{COOR}^{(2)}$	( a poly alkoxyated alkyl ethercarboxylic ester )
$-\text{CH}_2\text{COO}^-\text{M}^+$	( a poly alkoxyated alkyl ethercarboxylate )
$-\text{COR}^{(3)}$	( a poly alkoxyated fatty acid or a poly alkylene glycol ester )
$-\text{H}$	( a poly alkoxyated alcohol )

where  $R^{(2)}$  is selected from the group consisting of alkyl, alkylaryl, fatty alkyl of 1-30 carbon atoms,  $\text{M}^+$  is a counterion,  $R^{(3)}$  consisting of alkyl, alkylaryl, fatty alkyl and H.

12. A composition according to claim 11 in which the alkoxyated chain is formed of block copolymers.
13. A composition according to claim 12 in which the copolymers are mixed ethylene oxide / propylene oxide block copolymers.
14. A composition according to claim 11 in which  $\text{M}^+$  is a cation selected from the group consisting alkali and alkaline earths metal ions, ammonia and amines.
15. A composition according to claim 14 in which the base is selected from sodium hydroxide, potassium hydroxide, diethanolamine and triethanolamine.

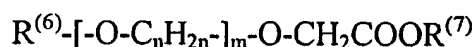
## 18

16. A composition according to claim 11 in which the poly alkylene glycol alkyl ether is selected from compounds of the formula :



where  $R^{(4)}$  and  $R^{(5)}$  are individually selected from the group consisting of H and alkyl of 1-10 carbon atoms, n is from 2-6 and m is from 2-10.

17. A composition according to claim 1 further including 3 to 25 % by weight of a poly alkylene glycol alkyl acetate of the formula :



where  $R^{(6)}$  and  $R^{(7)}$  are individually selected from the group consisting of H and alkyl of 1-30 carbon atoms, n is from 2-6 and m is from 2-10.

18. A composition according to claim 2 in which the aprotic solvent is selected from the group consisting of ethylene carbonate, propylene carbonate, dimethyl sulfoxide, N-methyl-2-pyrrolidinone and  $\gamma$ -butyrolactone.

19. A composition for removing paint from a substrate comprising in approximate parts by weight :

- 5 parts of oleyl ether carboxylic acid,
- 19 parts of triethylene glycol dimethyl ether,
- 25 parts of tetraethylene glycol dimethyl ether,
- 25 parts of polyethylene glycol dimethyl ether and
- 10 parts of dipropylene glycol monomethyl ether.

20. A composition according to claim 19 further including in approximate parts by weight :

- 5 parts of a polar aprotic solvent,
- 0.3 parts of a base and
- 0.5 parts of a hydroxyalkylated cellulose thickener.

21. A composition for removing paint from a painted surface comprising in approximate parts by weight :

- 5 parts of oleyl ether carboxylic acid,
- 82 parts of dipropylene glycol monomethyl ether,
- 12 parts of a polar aprotic solvent,
- 0.3 parts of a base and
- 0.5 parts of a thickener.

22. A composition according to claim 21 in which the base is triethanolamine and the thickener is hydroxypropyl cellulose.

23. A method of removing discrete portions of a coating material from a surface comprising the steps of :

Applying the composition of claim 1 to said portions for a time sufficient to release the bond of the portions to the surface and form a residue of the composition and the portions and removing the residue from the surface.

24. A composition according to claim 23 in which the discrete portions are a coating of paint and the residue is removed by applying water to the surface.

25. A method according to claim 23 in which the discrete portions are fingernail polish.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/14081

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 1/72, 1/722, 3/22, 3/44

US CL : 510/ 174, 200, 202, 212, 413, 414, 470, 488, 502, 506; 134/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/ 174, 200, 202, 212, 413, 414, 470, 488, 502, 506; 134/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- A	US 5,015,410 A (SULLIVAN) 14 May 1991, See Abstract; col. 2, lines 15-45, col. 3, line 40 to col. 4, line 25; col. 4, lines 35-52; col. 4, lines 52-69; col. 5, lines 15-30; col. 5, lines 35-65.	1-18, 23, 24 ---- 19-22
X ---- A	US 5,124,062 A (STEVENS) 23 June 1992, See Abstract; col. 3, lines 20-65; col. 3, lines 63 to col. 4, lines 15; col. 7, lines 10-55; col. 8, lines 53-69.	1-18, 23, 24 ---- 19-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

31 AUGUST 1998

Date of mailing of the international search report

20 OCT 1998

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/14081

**B. FIELDS SEARCHED**

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

search terms: oleyl ether carboxylic acid, n-methyl pyrrolidone, polyalkylen glycol alkyl ether, ether, hydroxypropyl cellulose